

## THE ROLE OF ELECTRONIC MECHANISMS IN SURFACE EROSION AND GLOW PHENOMENA

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### 1. Introduction

Surface erosion and surface glow are textbook examples of phenomena originating in electronic transitions initiated by energetic particle-surface and photon-surface interactions. In the low-earth orbit (LEO) environment, such electronic energy-surface interactions may be triggered by ultraviolet radiation, by electrons and ions, or by low-energy collisions with neutral atomic oxygen and nitrogen. These interactions are particularly efficient in dielectrics because of their capacity to absorb, localize and rechannel electronic energy in ways which lead to the desorption of atoms, molecules, ions and even clusters. And, in the LEO environment, virtually all materials present a dielectric surface to the ambient radiation flux.

Recent research has established that the dominant constituents in electronically induced surface *erosion* are ground-state neutral atoms and molecules. The next most important decay channel for incident electronic energy is through electronic desorption of excited neutral particles which decay radiatively in flight away from the surface -- thus causing a surface *glow*. The rates for both erosion and glow processes are strongly influenced by the presence of surface impurities, as well as by the nominal composition and thermal history of the surface -- all matters of significant concern for assessing the viability of spacecraft materials.

The experimental studies of desorption induced by electronic transitions (DIET) described in this paper are producing an increasingly complete picture of the dynamical pathways through which incident electronic energy is absorbed and rechanneled to produce macroscopic erosion and glow. These mechanistic studies can determine rate constants for erosion and glow processes in model materials and provide valuable guidance in materials selection and development. However, they are not a substitute either for simulations or lifetime studies. Instead, they provide likely clues to the tailoring of materials survive the rigors of the LEO environment, and indeed, establish the scientific context within which the meaning of the simulations and lifetime studies can be accurately assessed.

### 2. Historical Background

The first DIET experiments, beginning with the pioneering work of Menzel and Gomer [1] and of Redhead [2] in the 1960's, centered primarily on the detection of ions desorbed from surfaces by electrons. This work on electron-stimulated desorption (ESD) established the general understanding that these processes involved electronic excitation to a repulsive potential energy surface. A decade later, Madey and Yates showed that angular distributions of the desorbing ions could provide detailed information about the surface chemical bond [3]. By the late 1970's, the advent of synchrotron light sources had paved the way for photon-stimulated desorption (PSD) experiments and aroused renewed interest in these phenomena, particularly in dielectrics. The first model of a specific electronic desorption in a dielectric came from

Knotek and Feibelman [4], who showed that the unexpectedly large yield of  $O^+$  ions from  $TiO_2$  could be traced to a deep core-level excitation and localized hole-pair formation, leading to a "Coulomb explosion" that ejects the  $O^+$  ions from the near-surface layers.

However, it was clear that ESD/PSD of ions was not an efficient contributor to mass loss from irradiated materials. A new perspective on electronically-induced surface erosion was opened up in 1981, when Tolk *et al.* reported that the ESD yield of excited neutral alkali atoms from alkali halide crystals exceeded the ion yields by some five orders of magnitude [5]. Shortly thereafter, similar results were found in the photon-stimulated desorption of Li from LiF [6]. Since then, it has been established that the yield of *ground-state* neutral alkali atoms from alkali halides, in turn, exceeds the excited-state yields by another one to two orders of magnitude [7]. Efficient, electronically-driven desorption of neutral excited and ground-state atoms is now recognized as the dominant phenomenon whenever dielectric materials are irradiated by photons, electrons, metastable atoms or slow atoms or ions. However, neither the Knotek-Feibelman nor the older Menzel-Gomer-Redhead models can account for the large neutral ESD/PSD yields, so an adequate theory is still under development. At present, then, the search for mechanistic explanations of glow and erosion in the LEO environment must take its cues heuristically from DIET experiments on model materials.

## 2. Neutral Species Desorption Spectroscopy

A typical neutral-species desorption experiment is configured as in Figure 1. The incident radiation -- photons, electrons, or heavy particles -- desorbs ground- or excited-state atoms and molecules from the sample surface, which is maintained under ultrahigh vacuum conditions (nominally  $10^{-10}$  torr) to allow control of surface contamination. The particles ejected from the surface radiate as free particles as they pass through the region in front of the surface. That radiation is imaged by a focusing lens system through the slit of a spectrometer and onto the

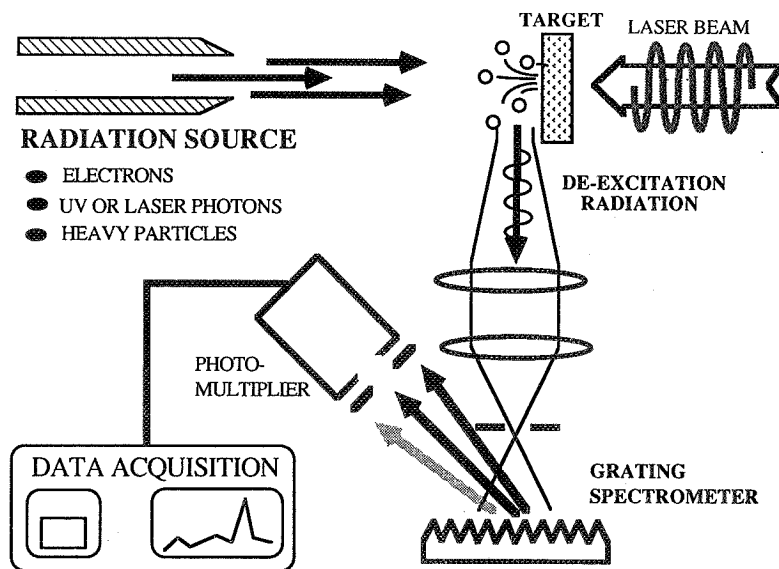


FIGURE 1

*Schematic of an experiment using neutral species atomic and molecular spectroscopy to study DIET processes.*

entrance port of a photomultiplier tube. Ground-state neutrals are made to fluoresce by the use of a dye laser tuned to the transition frequency of a resonant transition in the species to be identified. By scanning the spectrometer through the appropriate range of wavelengths, radiation from the desorbing species can be identified and relative yields quantified by integrating the spectral lines for each identified atom or molecule. On the other hand, if one wishes to measure velocity distributions, one scans the laser through the range of frequencies appropriate to the Doppler-shifted transition of interest; the atoms absorb at the appropriate Doppler-shifted frequency appropriate to their rest frame, and the de-excitation radiation, when plotted as a function of frequency, reflects the velocity distribution of the desorbing particles. Further details of these optical techniques have been described elsewhere [8].

Typical results from a spectrometer scan in such an experiment are shown in Figure 2. The samples of NaF and NaCl were maintained in ultrahigh vacuum, and cleaned prior to electron irradiation by heating for several hours. However, even with this cleaning procedure, there were impurities (H, OH and some unidentified species with a vibrational spectrum reminiscent of molecular radiation) still on the surface which desorbed along with the Na atoms from the substrate.

One of the points of interest in this spectrum is that the amplitude of the Na line is larger relative to the hydrogen lines in the NaCl spectrum. This suggests that desorption of the substrate atoms is less efficient in NaF -- in other words, that the presence of hydrogen or hydrocarbons on the surface may affect the possibility of electron-induced erosion. The vibration-like bands at the right edge of each spectrum have also become objects of considerable interest, since its presence appears to be correlated with a reduction in the desorption efficiency for substrate atoms [9]. It thus appears to be associated with the existence of a protective overlayer whose structure and composition are being investigated in more detail at the present time.

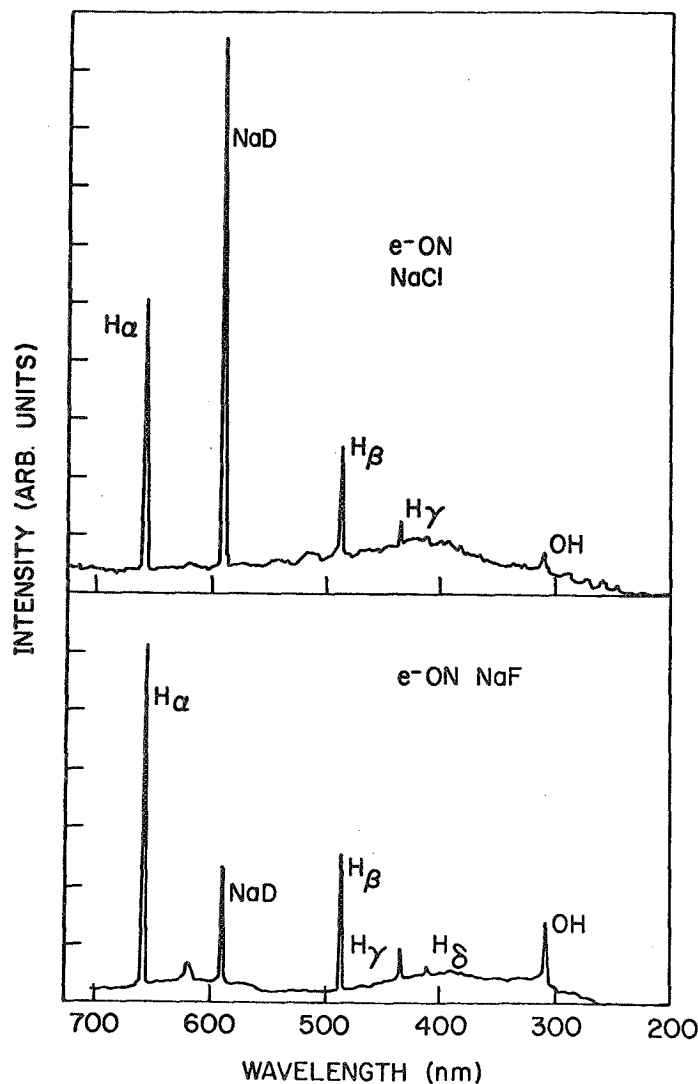


FIGURE 2

Typical spectrometer scans for the experimental geometry of Figure 1 in an ESD experiment on NaF and NaCl single crystals. Note the difference between the relative yields of the desorbing H and Na<sup>0</sup> atoms for the two different substrates.

#### 4. Photon-Stimulated Desorption Thresholds

The experimental PSD data, typified by those of Figure 3, indicate that there is a broad range of electron and photon energies over which the alkalis are desorbed with significant efficiency from alkali halides by ESD/PSD. In the Figure, the yield of neutral sodium atoms produced by photon bombardment of an NaCl single crystal surface is shown as a function of photon energy. The curve shows some structure at the levels of the 2p and 2s sodium core energy levels, but in general is rather featureless. This result is not surprising in view of the dominant role of defect diffusion in the PSD process for ground-state neutrals (see below). Similar results have been seen for a number of other alkali halides, including NaF, NaCl, NaBr and NaI [10].

However, as Townsend pointed out in his pioneering paper in ESD on alkali halides [11], if the creation of a self-trapped exciton is the first step in electronically stimulated desorption, one needs only the energy required to create the exciton on the dihalide molecule  $(X_2)^*$  to initiate the process (typically a few eV). However, nearly all measurements of the stimulated desorption process to date have relied on electrons or uv photons of significantly higher energies than the few electron volts mandated by this requirement. Moreover, until the development of the sensitive optical techniques necessary for tracking neutral desorption, it was not necessarily easy to look for the onset of desorption yields.

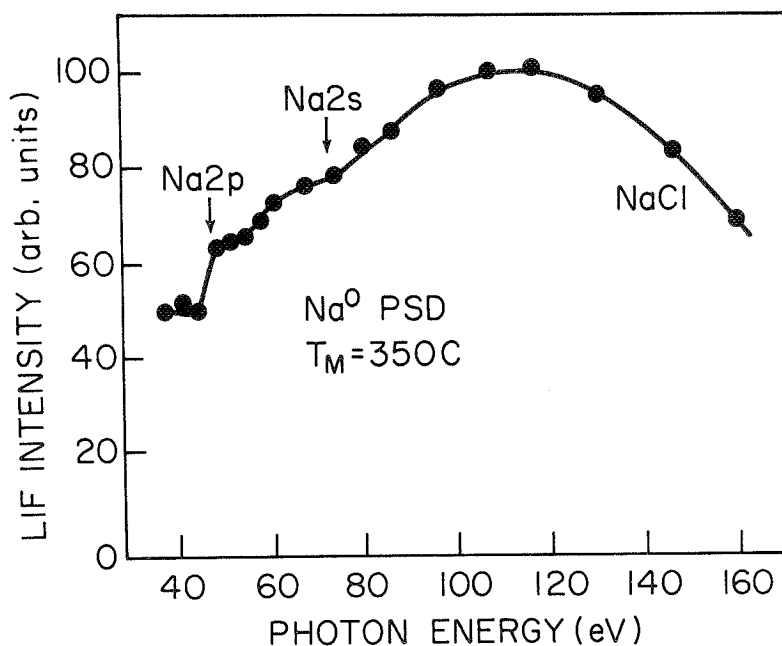


FIGURE 3

*Yields of neutral Na atoms in a PSD experiment on an NaCl crystal in ultrahigh vacuum. The yield, in arbitrary units, is plotted as a function of the photon energy in eV. Overall PSD efficiency for these experiments is a few per cent for  $Na^0$ .*

Recent measurements using filters to block out different portions of the incident uv photon energy spectrum show that the threshold for PSD of  $Li^0$  from LiF is indeed to be very low. Three spectral bins were chosen: from 0-13.2 eV (LiF filter), 20-90 eV (Al filter), and 0-200 eV, this last representing the full zeroth order spectrum transmitted through the toroidal grating monochromator (TGM) used in this set of measurements. The relative yields were calibrated by the convolution of the raw yield with a trapezoidal-rule integration of the measured response of a gold photodiode to the tuned spectrum of the TGM. After deconvolution of the monochromator efficiency from the raw data, it was found that that some twenty-five *per cent* of the total neutral yield results from photons with energies below the band gap for the LiF filter. This means that such desorption is likely to take place efficiently not only throughout

the spectral range of the primary ultraviolet photons found in LEO, but also that low-energy photons produced in secondary processes may also produce significant effects. The low value of this neutral emission threshold is consistent with results obtained by Schmid *et al.* almost a decade ago using four-photon excitation from a pulsed ruby laser [12]. However, the present results indicate that the process leading to alkali desorption is *not* intrinsically intensity dependent, as the earlier laser results might have led one to believe.

Experimental studies of the thresholds and energy dependence for electron bombardment of alkali halides indicate that the same general picture holds for ESD. For purposes on estimating rates to, say, within an order of magnitude, it is appropriate to assume that the efficiency for ESD/PSD processes producing ground-state neutral alkalis from alkali halides is on the order of a few *per cent*, while the excited-state alkalis are produced with one to two orders of magnitude less efficiency.

#### 4. Temperature Dependence of Electron-Stimulated Desorption Processes

Measurements of desorption as a function of sample temperature can give indications of the degree to which diffusion or other thermally activated processes play a role in desorption [13]. Figure 4 shows a measurement of the fluorescence yield as a function of temperature for  $\text{Li}^0$  and  $\text{Li}^*$  desorbed from the (100) face of a LiF crystal under electron irradiation at an energy of 750 eV. The plot shows that the desorption follows the classic Arrhenius curve, but a logarithmic plot of the data shows two slopes, with activation energies of 1.29 and 1.61 eV, respectively. This may be due to the difference between "direct" desorption of  $\text{Li}^0$  following depletion of the halogen on the surface layer and the agglomeration of weakly bound alkali atoms, on the one hand, and for "indirect"  $\text{Li}^0$  desorption mediated by diffusion-driven defect migration from the near-surface layers of the bulk material, on the other. At the highest temperatures for which measurements were made, the saturation of the yield curve suggests an equilibrium between the defect production and desorption rates.

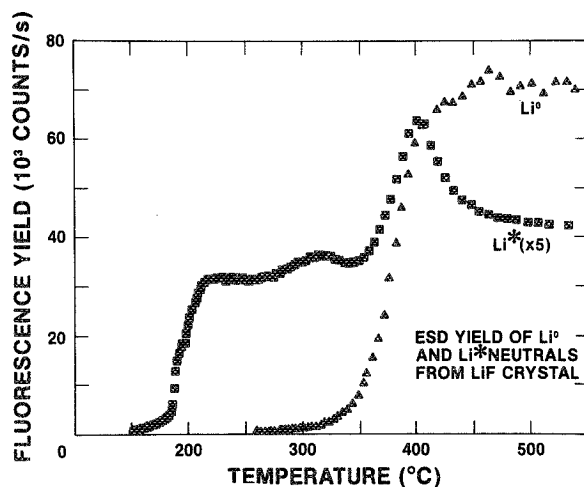


FIGURE 4

*Measured yields of  $\text{Li}^0$  (triangles) and  $\text{Li}^*$  (squares) desorbed by electron bombardment from the surface of an LiF crystal in ultrahigh vacuum. The electron energy was approximately 750 eV. The  $\text{Li}^*$  experiment was done in a different geometry than that for  $\text{Li}^0$ , so that the relative yields cannot be compared from the figure.*

Collateral evidence for the thermal character of ground-state neutral desorption comes from the experimental determination of velocity distributions as a function of surface temperature. Similar results have been obtained for ESD measurements on NaCl and for PSD experiments on NaF, NaCl, NaBr and NaI [11]; in both experiments, it was found that the measured surface and best-fit temperatures were coincident and completely consistent with neutral ground-state alkalis desorbing in thermal equilibrium with the surface.

While the ground-state neutral alkalis exhibit features typical of thermally-desorbed atoms, the excited-state alkalis show characteristics quite at variance with this picture. First of all, the onset in the Li excited-state yield occurs at temperatures far below those necessary to desorb ground-state neutral Li (Figure 4). Moreover, the behavior of the curve above 250° C certainly does not resemble thermal desorption (Arrhenius curve with saturation) as is the case with the Li<sup>0</sup>. PSD measurements of Na<sup>\*</sup> from NaCl show a contrary behavior: The excited state yield *falls off* strongly with temperature in the region where the ground-state yield is increasing most steeply [14]. This behavior may be indicative of fundamental differences between electron- and photon-initiated processes, or it may reflect the short-pulse character of the excitation from the synchrotron radiation source. In any case, however, it is apparent that strongly non-thermal behavior is a general feature of DIET processes leading to the formation of *excited* neutrals.

Although the relative yields of ground-state and excited-state neutrals appear to be within an order of magnitude of each other in Figure 4, the ground-state data were obtained with the laser configured for Doppler spectroscopy, and therefore the fluorescence yields may not reflect the true density of Li<sup>\*</sup> relative to Li<sup>0</sup> in the focal volume of the spectrometer. This relative yield may provide important clues to the strength of the desorption mechanism.

## 5. Time Dependence of Electron-Stimulated Desorption

The spectroscopy of excited-state neutrals shows other features which differ sharply from the results of studies on ground-state neutral desorption. For example, measurements of excited-state fluorescence yields as a function of distance from the sample surface for ESD of Na from NaCl have generally been consistent with a kinetic energy of several eV, rather than the thermal velocities characteristic of the ground-state neutrals [9]. Also, time-resolved measurements indicates that another difference between ground-state and excited-state neutral alkali desorption is that the former result from a combination of surface and near-surface-bulk excitations -- mediated by diffusion of electronic defects from the near-surface bulk -- whereas the latter appear to be produced at the crystal surface.

Figures 5 and 6 display the results of time-resolved ESD experiments on LiF which contrast the desorption characteristics of Li<sup>0</sup> and Li<sup>\*</sup> for the same electron-gun and temperature parameters. In this case, the temperature of the LiF surface was maintained at 400 C, and the gun was chopped at a rate of a few kHz. The laser-induced-fluorescence (LIF) yield was measured for the ground-state Li, and then the laser was turned off to measure the yields of Li<sup>\*</sup>. In Fig. 5, the LIF yield for Li<sup>0</sup> is shown as a function of time for a pair of electron gun pulses. The yield climbs sharply at first, and then shows a gradual saturation as the contribution from near-surface bulk layers increases. When the electron gun is turned off, the LIF yield is observed to drop sharply at first, and then fall quite slowly until the next electron-gun pulse is turned on. In Fig. 6, on the other hand, the Li<sup>\*</sup> yield rises on the leading edge of the incident electron pulse just as Li<sup>0</sup>, but turns off instantaneously with the trailing edge of the exciting electron beam. Indeed, a measurement of this trailing edge of the Li<sup>\*</sup> fluorescence pulse with the best time resolution possible with our multichannel analyzer (10<sup>-7</sup> s) showed that the yield decreases from 0.9 to 0.1 of its maximum value within 100 ns. This means that while the *source* of Li for excited-state Li is the same as that for the ground-state Li, the excitation *mechanism* yielding Li<sup>\*</sup> must be distinctively different.

The ground-state data are well described by a diffusion model based on realistic electron-energy deposition profiles [15, 16]; preliminary indications are that such a model will be appropriate for describing ground-state PSD of alkalis from alkali halides as well. Similar

behavior is observed for PSD of  $\text{Li}^0$  and  $\text{Li}^*$ , but in this case the time delays for emission of ground-state neutrals are on the order of *seconds* rather than milliseconds.

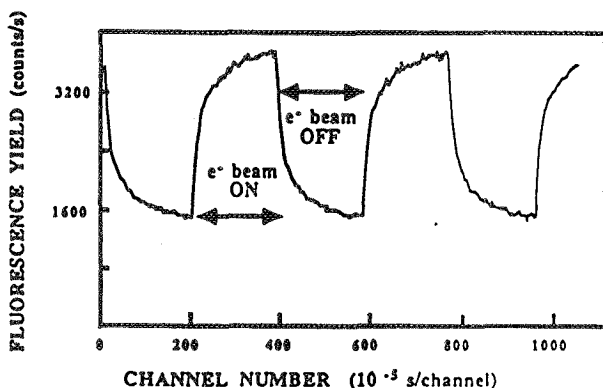


FIGURE 5

*Fluorescence yield as a function of time for  $\text{Li}^0$  desorbed by electron bombardment of the LiF (100) surface.*

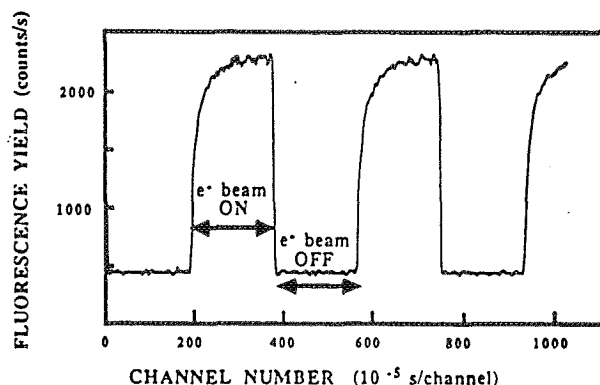


FIGURE 6

*Fluorescence yield as a function of time for  $\text{Li}^*$  desorbed by electron bombardment of the LiF (100) surface.*

## 6. A Model for Defect-Induced Desorption

Electronically stimulated desorption of ground-state neutral alkali atoms from alkali halide crystals exhibits a variety of features consistent with thermal desorption: a nearly Maxwellian distribution of velocities, a characteristic Arrhenius desorption characteristic as a function of surface temperature and a yield vs. bombarding energy characteristic which shows relatively little structure at the known locations of alkali core-hole excitation energies. Differences between ground-state ESD and PSD yields probably reflect, as much as anything, the fact that ESD tends to be a one-step process where PSD can have multi-step effects, including the production of secondary electrons which themselves are capable of effecting ESD. In addition, the time-resolved measurements indicate that diffusion plays a significant role, especially at high temperatures [15].

On the other hand, it has been shown that halogens desorbed from alkali halides under low-energy electron bombardment have suprathermal energies and are emitted preferentially along the halogen "strings" in the crystal [11]. This suggests that the formation and relaxation of H-centers is a likely mechanism for the ejection of the halogens from the surface and near-surface layers of the bulk. This picture is reminiscent of the focussed collision sequence originally proposed by Pooley [17] and Hersch [18], and involves the formation of an H-center (the so-called "crowdion," -- a pair of halogens on a single halogen site) leading to preferential and energetic ejection of halogens along the  $\langle 110 \rangle$  directions. Simultaneously, by leaving behind an electronic defect and an electron free to bind to the now undercoordinated alkali atoms near the surface (F-center), it provides a mechanism for the generation of neutral alkalis for thermal desorption.

No such simple picture appears possible for the excited-state alkalis, however. To begin with, there is the distinctly non-thermal desorption characteristic already discussed. Also, time-resolved measurements of ESD for excited-state neutrals shows that the yield of these species drops to background level within 0.1 ms of the turn-off time of the electron gun.

Moreover, the fact that excited-state neutral yields are typically two to three orders of magnitude larger than the ion yields indicates that the mechanism must also be relatively simple compared to the Knotek-Feibelman picture involving inter-atomic Auger processes. Finally, there is the fact that only the first excited state of alkalis desorbed from alkali halides has ever been observed for low incident electron energies -- in contrast to the case of hydrogen, for example, where three or four excited states are routinely observed in ESD and PSD experiments (see Figure 2).

Thus recent experiments on ESD and PSD of *ground-state* neutral alkali desorption in the alkali halides appear to confirm early inferences pointing to the formation of self-trapped excitons followed by thermal desorption due to "halogen exhaustion" and defect migration. This sequence of events is representative of a perfectly general mechanism in which the formation of an exciton (electron-hole pair) is followed by relaxation to a mobile, permanent electronic defect whose diffusion leads to selective bond-breaking. Our fascination with the alkali halides as a particularly tractable model material should not be allowed to obscure the more important fact that this generic mechanism operates in many other materials, including many metal oxides, the alkaline earth halides, fused silica and many glasses [19].

## 7. Electronic Transitions and the Atomic Oxygen Problem

Now, after all these preliminaries, the question must be asked, what has all this got to do with the problem of oxygen-atom-induced erosion the low-earth-orbit environment? The relevance of electronically induced erosion and glow can be considered under at least three headings: changes in surface composition induced by electron bombardment or UV- photon irradiation in LEO; electronic transitions experienced by the oxygen atom in gas-surface collisions; and possible synergistic or catalytic effects of oxygen, electrons and solar ultraviolet radiation.

Given the efficiency of defect-induced desorption processes, it is clear that electronic mechanisms will play a significant role in the alteration of surface composition and stoichiometric properties. Spacecraft surfaces in LEO are exposed to significant electron and UV photon flux. The fluences is of order  $10^{11-12}$  electrons (photons)/cm<sup>2</sup>/sec and the spectrum of both electrons and photons is hard enough to produce ESD and PSD in dielectric materials.

Systematic ESD/PSD experiments on hydrocarbons, polymers, composites and plastics have not been carried out, although it is known that H is desorbed efficiently by both electrons and photons from condensed hydrocarbons [20]. In the case of hydrogen-bearing materials, if there is a significant differential loss of H<sub>2</sub> and/or H, this could change the reactivity of O(<sup>3</sup>P) with the surface, due to the well-known propensity of this atom to replace hydrogen when it is energetically favorable to do so. Such substitutional events are likely to impact mechanical integrity and alter the electrical and thermal properties of spacecraft material.

Also, in many materials -- alkaline earth halides, alkali halides and metal oxides, for example -- the ESD/PSD events trigger the accumulation of metallic overlayers on the surface which are likely to become oxidized rapidly, again with the likelihood that desirable electrical, optical or thermal properties will be altered. Composites and glasses, with their many and various electron traps, are likely to be particularly difficult to understand -- but their susceptibility as a class to electronically induced radiation damage of this type is well known.

There is at present little or no guidance from either physics or chemistry for predicting quantitatively how electronic transitions will affect the collisions of 5 eV oxygen atoms with



surfaces, although initial measurements using a 2.5 keV beam of atomic oxygen show definite differences between oxygen ions and atoms in measured desorption spectra. Gas-surface interactions with molecular beam sources of the purity requisite for mechanistic studies are generally too low in energy to allow for easy projection of low-energy mechanisms to the 8 km/s characteristic of LEO conditions. In addition, given that the heat of formation of many oxides is on the order of 5 eV, it is quite possible that there are strong threshold effects which make the extrapolation upward from molecular beam energies problematical. Most sputtering theories deal solely with metallic materials, where the collision cascade is the dominant mechanism. However, there is a wealth of evidence showing the importance of electronic mechanisms in the sputtering of insulators and semiconductors, even at relatively high energies. If electronic surface-interaction channels are open, even at low energies, it is unlikely that surface phonon excitations -- prominent though they are in meV noble-gas scattering from surfaces -- play a significant role. Indeed, the demonstrated reactivity of O on many surfaces argues against significant coupling to the surface phonon spectrum.

Two phenomena which are likely to contribute to both erosion and glow through radiation-induced electronic excitations are *level-crossing*, on the one hand, and *coupling to defect and impurity states* in dielectric materials, on the other. Space allows only a brief consideration of these two situations.

Level crossings, or curve crossings, as they are also known, occur in adiabatic collisions, and allow two colliding atoms A and S to experience electronic transitions such that one partner in the collision is left in an excited electronic state. Should atom S (for "substrate") be localized in a repulsive energy state, it would be ejected from the material and radiate as a free atom (or molecule) exterior to the material surface -- thus producing erosion and/or glow. In the case of an incident oxygen atom, the electronic energy can be transferred to an ejected surface constituent atom, retained by the bombarding atom as it scatters from the surface, or be absorbed by a molecule (NO, for example) formed in the collision of the oxygen with atoms already on the surface -- depending on the particular features of the atomic-oxygen-induced chemistry.

Coupling between electronic states of an incident atom A and those of surface atoms S can occur because of overlaps between empty states of the atom and filled defect or impurity states in the surface band structure. The energetics are shown schematically in Figure 7. These defect or impurity states occupy levels in the middle of the band gap which would exist in the bulk: the defect states because of the abrupt termination of the bulk material -- in effect, creating a defect located immediately adjacent to every surface atom -- and the impurity states because they likewise cannot occupy any of the electron levels in the filled valence bands of the pure material.

Either of these two types of electronic transitions is capable of producing excited atoms whose radiative decay appears as a surface glow. Ground-state neutral atoms and molecules can also arise efficiently from the operation of either mechanism -- and such neutrals can, as in the Pooley-Hersh model, either be expelled energetically from the material or exist in an unbound configuration susceptible to thermal desorption. Thus the oxygen collisions with the surface can, through the operation of purely electronic mechanisms, give rise to surface erosion. Moreover, synergistic effects, such as those already observed in various LEO experiments, fit neatly into this picture, since the ambient ultraviolet and electron irradiation can change both surface composition and stoichiometry in ways which exacerbates the effects of the atomic oxygen.

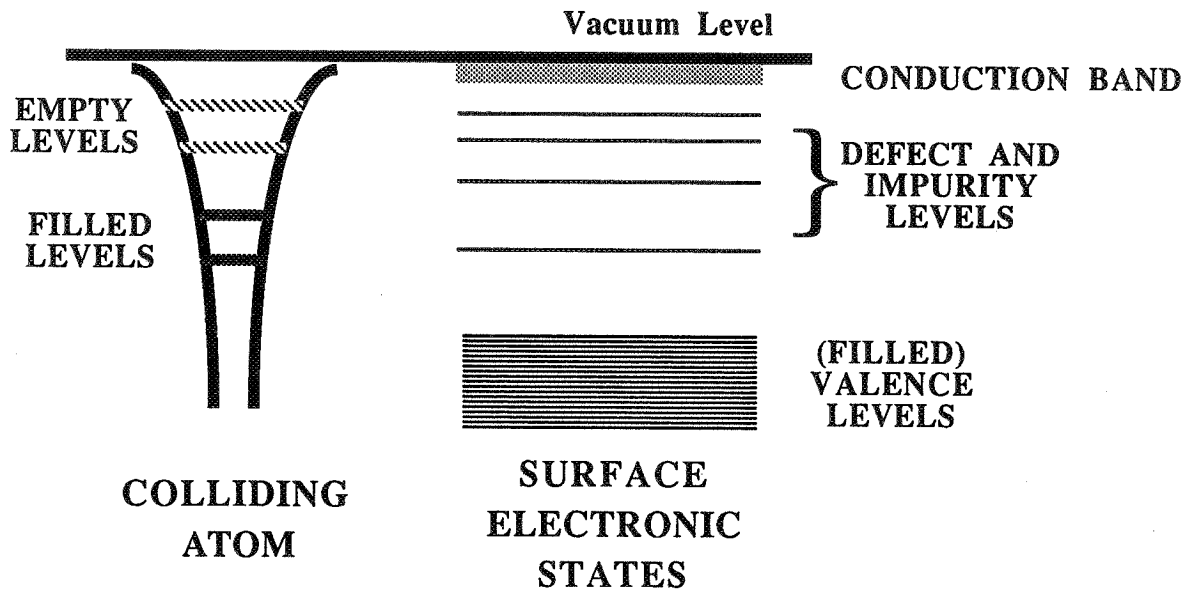


FIGURE 7

*Schematic drawing of energy levels for an atom colliding with a surface.*

## 8. Conclusions

Extensive experiments with electron, photon and heavy particle irradiation of alkali halides and other simple model materials have produced a large body of evidence showing that:

- Surface erosion, consisting primarily in the ejection or desorption of ground-state neutral atoms, occurs with large efficiencies for all irradiating species.
- Surface glow, resulting from the radiative decay of desorbed atoms, molecules and clusters in excited electronic states, likewise occurs for all irradiating species.
- The typical mechanism for ground-state neutral desorption is exciton formation, followed by relaxation to a permanent, mobile electronic defect which is the precursor to bond-breaking in the surface or near-surface bulk of the material.
- The mechanisms for excited-atom formation may include curve crossing in atomic collisions, interactions with surface defect or impurity states, or defect diffusion, and are still a subject of active investigation. The phenomena are not explainable at the present time by any physical model.
- The generic features of desorption induced by electronic transitions are characteristic of a broad class of dielectric materials, many of which are important to the construction of space platforms and satellites.

It is only to be expected that further mechanistic studies, particularly those involving the use of atomic oxygen beams at energies typical of the LEO interaction energy, will turn up further interesting examples of the influence of electronic transitions on erosion and glow phenomena.

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